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Published in:
Macromolecular Theory and Simulations

DOI:
10.1002/(SICI)1521-3919(19980301)7:2<211::AID-MATS211>3.0.CO;2-A

Extended conformations of isolated molecular bottle-brushes: Influence of side-chain topology

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(Received: July 4, 1997; revised manuscript of August 28, 1997)

SUMMARY: A Monte Carlo study is presented to discuss the influence of the side-chain topology on the enhancement of the persistence length of a molecular bottle-brush in a dilute athermal solution due to the excluded volume interactions between the side chains. The structures investigated consisted of freely jointed backbones of 100 hard spheres (beads) of diameter 1 to which 50 equally flexible side chains were grafted. The diameter of the side-chain beads was varied from 1 to 3 in the same units. For every given size of the side-chain bead, the length of the side chains was varied from 4 to 20 beads. The ratio between the persistence length and the bottle-brush diameter, which is the determining factor for lyotropic behavior of conventional semi-flexible chains, was found to be almost independent of the side-chain length. At the same time, it was found to increase considerably with increasing size of the side-chain beads, suggesting that by a proper choice of the chemistry lyotropic behavior of molecular bottle-brushes due to excluded-volume interactions between the side chains might be achieved. Moreover, relatively short side chains can be used since the side-chain length has only a minor influence on the ratio between the persistence length and the diameter. These findings are in a good agreement with recent experimental observations.

Introduction

Recently, there has been a growing interest in so-called molecular bottle-brushes, defined as comb copolymers with a high density of side chains[1–14]. Molecular bottle-brushes may have many special properties, such as lyotropic behavior in a dilute good solvent as well as highly ordered microphase separated structures in the melt[14]. Another interesting aspect is that the attachment between the side-chains and the polymer backbone may be covalent, but a strong association between end-functionalized oligomeric chains and homopolymers also suffices. In the latter case, self-assembled mesomorphic structures in the melt or concentrated solutions are formed only if the association is strong enough to prevent macrophase separation and if the backbone side chain repulsion is sufficiently strong to induce microphase separation. In the case of covalently linked side chains, macrophase separation is obviously not possible.

The conformations of isolated molecular bottle-brushes are directly related to the solvent quality. Of special interest is the case of a good solvent for the side chains, in which case the side chains effectively repel each other leading to extended conformations. In this work, we focus on the equilibrium conformations of isolated molecular bottle-brushes, assuming a good athermal solvent and covalent bonding of the side chains. Important parameters are the persistence length λ of the backbone, defined as the characteristic length over which a chain section remains straight, and the diameter D of the bottle-brush. Since longer side chains have a stronger net excluded-volume effect, the persistence length is expected to increase as a function of the side-chain length, M. However, concerning the possibility of lyotropic behavior of bottle-brushes in a dilute solution, the critial parameter is the ratio between λ and the diameter, D, of the molecule. For semi-flexible polymers this ratio has to be of the order of 10 or more ($\lambda/D > 10$) in order to lead to lyotropic behavior[15,16]. Theoretically, opinions agree on the qualitative statements that both λ and D increase steadily with increasing side-chain length M, however, they vary considerably as far as their ratio is concerned. According to Birshtein and co-workers[17], the ratio should be independent of the side-chain length, whereas Fredrickson[18] came to the conclusion that $\lambda/D \propto M^{9/8}$ implying that the required extension can be achieved simply by increasing the side-chain length.

These conflicting opinions prompted us to investigate molecular bottle-brushes by computer simulations. In a recent paper[19], we demonstrated, using a 3d continuous space Monte-Carlo model, that for an isolated molecular bottle-brush, where the freely jointed beads of the main chain and of the side chain have identical size, the persistence length indeed increases considerably due to excluded-volume interactions, however, the ratio λ/D

 CCC 1022-1344/98/$15.00

remained nearly constant (in the regime studied) as a function of the side-chain length, thus supporting the predictions by Birshtein and co-workers[17]. Moreover, for the model studied, this ratio was not nearly large enough to satisfy the inequality required for lyotropic behavior of semi-flexible chains.

Experimentally, the recent results of Schmidt and co-workers[1–3] are directly related to this issue. They succeeded in polymerizing bottle-brushes consisting of polymethacrylate (PMA) backbones together with covalently bonded oligostyrene side chains ($700 \leq \overline{M}_n \leq 5000$ g/mol). Using dynamic light scattering and X-ray scattering techniques, they noticed that for dilute solutions in a good solvent, toluene, the chains adopt extremely extended conformations characterized by a persistence length of up to $\lambda \approx 1000$ Å. For polymer concentrations of 30 wt.-% and higher, they observed a very narrow X-ray scattering peak which was interpreted as evidence that a nematic solution was obtained. Therefore, our computational results[19] seem to contradict these experimental results[1–3]. However, there are important differences between the system studied by Schmidt and co-workers and the computer model we used. First of all, the size of the styrene side-units is undoubtedly bigger than the size of the methacrylate monomers making up the backbone and, secondly, both backbone and side chains are already considerably stiffer than freely jointed chains. Moreover, and this could be the main factor, the number of side chains per Kuhn segment of the backbone is considerably larger than in our case. As a consequence, the effective excluded-volume interactions between the side chains is also considerably larger. One way of achieving a larger excluded-volume effect for the computer simulations as well is by selecting the same number of side chains as before, however, with side-chain beads which are larger than the backbone beads. The results of this endeavour are presented here.

Simulation method and model

Monte Carlo (MC) simulations were used to study the conformations of molecular bottle-brush copolymers. The model used is described in detail in our previous paper[19]. All the structures were modeled in continuous 3d space as linear chains of hard spheres (beads) freely jointed together, to which side chains consisting of beads of a given size are grafted. In this study, the diameter of side-chain beads was set equal to 1.0, 2.0, 2.5 and 3.0, whereas the diameter of the main-chain beads in the same units equals 1.0. The only constraint in the system is the non-overlapping condition and, therefore, the potential energy takes the form:

$$U_{ij} = \begin{cases} 0 & \text{if } i \text{ and } j \text{ are neighbours or } r_{ij} > 0.5 \cdot (d_i + d_j) \\ \infty & \text{otherwise} \end{cases} \quad (1)$$

where r_{ij} is the distance between beads i and j, d_i and d_j are the corresponding diameters of the beads (i.e., for the main-chain beads $d_{main} = 1.0$ and for the side-chain beads $d_{side} = 1.0$, 2.0, 2.5, or 3.0, however, for a given bottle-brush d_{side} is the same for all the side-chain beads). The distances between the centers of mass of connected (neighbour) beads i and j was always set to the minimum possible, i.e. to $0.5 \cdot (d_i + d_j)$. The hard sphere character of the model simulates a good, athermal, solvent.

Configuration space is sampled according to the Metropolis importance-sampling scheme[20]. Firstly, for every trial step it is decided whether it is attempted to move a main-chain bead or a side-chain bead. The probability of trying to move a main-chain bead is given by[19]

$$p = \frac{N^3}{n_s M^3 + N^3} \quad (2)$$

where N is the number of main-chain beads, M is the number of beads per side chain, and n_s is the total number of side chains. After that, a bead is chosen randomly from the main-chain beads or from all the side-chain beads. The trial move then consists of a rotation of the bead over a randomly chosen angle around the vector defined by the neighboring beads. This procedure can be considered as an off-lattice variant of the microrelaxation (L-flip in a lattice) first introduced by Verdient et al.[21] In the case of a grafted main-chain bead, also the side chain connected to it is rotated. This type of motion refers to the ideas of the pivot algorithm[22] which has been studied for linear chains both in cubic[23] and tetrahedral[24] lattices and in continuous space[25]. The three different trial-move types concerning rotations of "common beads", "grafted main-chain beads", and "chain-end beads" are illustrated in Fig. 1. The trial move is accepted if the new position of the beads does not violate the non-overlapping requirement, otherwise it is rejected.

The structures studied consisted of 100 main-chain beads (99 chain segments) of diameter 1.0 carring 50 side chains of M beads of diameter 1.0−3.0 each. The main-chain beads from which a side chain is grafted were chosen equally along the backbone, i.e. every other main-chain bead carried a side chain. Side chains of lengths M = 4, 6, 8, 10, 12, 16 and 20 were considered together with side-beads of diameters 1.0, 2.0, and 3.0. For the side-bead diameter 2.5, only the structure with 50 side chains of length 20 beads was considered. Every bottle-brush structure was first equilibrated by running the simulation for at least $5 \cdot 10^5$ MC main-chain steps and $50 \cdot M^2$ MC side-chain steps. For the main-chain, one MC step corresponds to 100 ($=N$) attempts, whereas for the side chains it corresponds to $50 \cdot M$ attempts. After equilibration steps, the simulation was divided into 10 blocks, each consisting of $100 \cdot N^2$ MC main-chain steps ($=10^6$ MC steps) and $100 \cdot M^2$ MC side-chain steps. The aver-

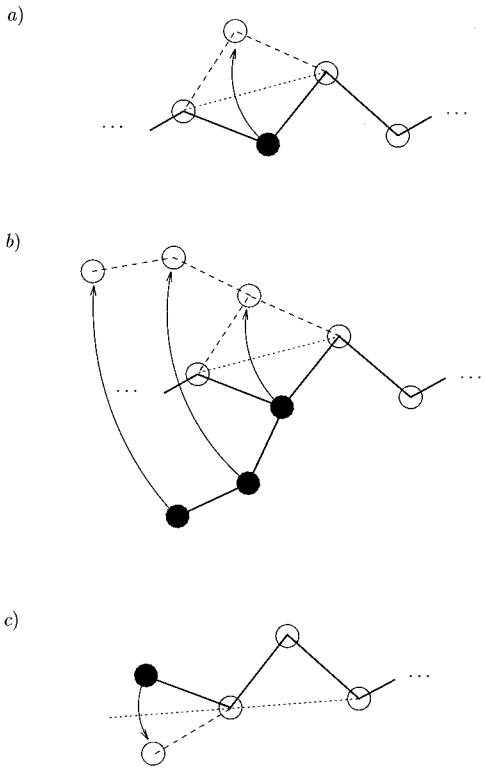

Fig. 1. Illustration of Monte Carlo moves. (a) Bead that is neither an end bead, nor a main chain bead connected to a side chain. (b) Main chain bead connected to a side chain. (3) End bead

age value of the quantity of interest $\langle A \rangle$ was estimated as an average of the block averages $\langle A \rangle_{block}$, each of which was calculated using 500 conformations taken from the simulation block at equally spaced intervals.

Results

In this section, we present the results of our Monte-Carlo simulations on bottle-brushes consisting of a main chain of 100 beads of size (diameter) 1.0 linked with 50 side chains of 4−20 beads of size 1.0−3.0. To suppress the chain-end effects, which might become more important as the side-chain size increases, we excluded 5 main-chain beads from both chain ends and all the beads of the side chains connected to these beads. Therefore, the structure we actually focus on consists of a main chain of 90 beads and 45 side chains of a given length and size. However, when taking Monte-Carlo steps, all the beads (whether included or excluded) were treated equally.

To discuss the possibility of lyotropic behavior of bottle-brushes, we have to study the ratio between the persistence length and the bottle-brush diameter and, therefore, the definition of these quantities becomes essential. As previously demonstrated[19], a correct description of the bottle-brush backbone requires at least two characterictic lengths: at a small length scale the backbone behaves quite flexibly, while the extension occurs at a larger length scale. Consequently, the expressions of the worm-like chain model[26], relating the persistence length to the radius of gyration, underestimate the persistence length we are really interested in. A better way is to use instead the relation between the persistence length and the bond-angle correlation function, which is given by

$$\langle \cos\theta(s) \rangle = \mathrm{e}^{-s/\lambda} \tag{3}$$

where $\langle \cos\theta(s) \rangle$ is the average cosine of the angle between chain segments separated by a length s.

Fig. 2 shows the bond-angle correlations for selected bottle-brushes (for clarity only for M = 4, 6, 10, 20) hav-

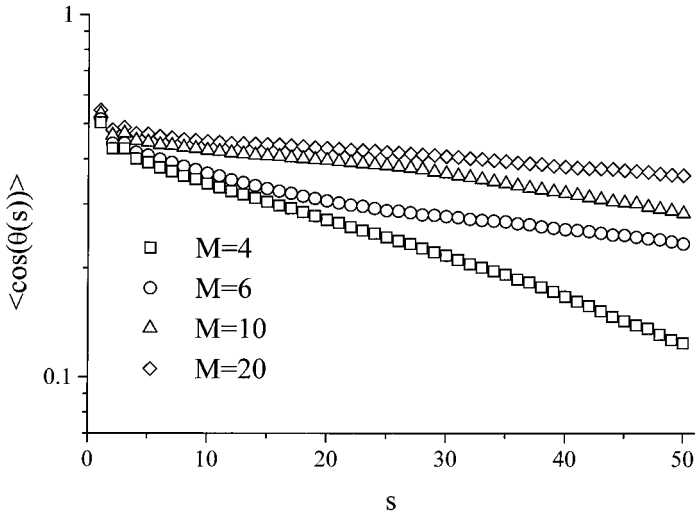

Fig. 2. Bond-angle correlations $\langle \cos\theta(s) \rangle$ as a function of the separation, s, of the main-chain beads for side-chain lengths M = 4, 6, 10, 20 of structures with side-bead size 3.0

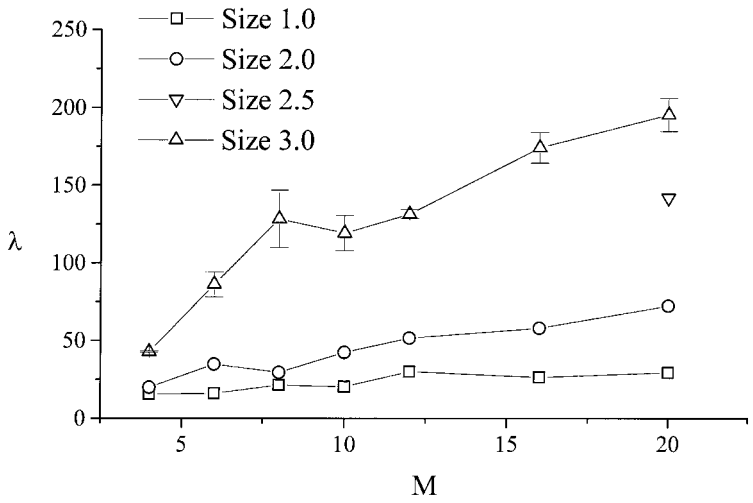

Fig. 3. Persistence length λ of the bottle-brush backbone obtained by using the bond-angle correlation data. The error bars due to the fitting are smaller than the symbols used to present the data, unless specifically shown

ing the diameter 3.0 for the side-chain beads. Although not shown, the same data were calculated for structures having side-bead diameters of 1.0, 2.0, and 2.5. The most appropriate estimate for the persistence length is obtained by using the middle linear parts (we choose $10 < s < 40$) of the curves. This type of fitting leads to the values presented in Fig. 3. The error bars shown include only the errors due to the fitting of the given functional form to the data since the other sources of inaccuracy are difficult to estimate. The data show a steadily increasing behavior of the persistence length as a function of both the side-chain length and the side-bead size. It can be seen that the persistence length exceeds the contour length of the bottle-brush backbone, being a strong indication of the side-chain induced stretching, for structures having more than 6 beads of diameter 3.0 per side-chain. The most reliable estimates are the ones obtained for the larger values of M since then the contribution of the self-avoiding character of the backbone conformation is less important. Although the exact scaling of the persistence length as a function of M cannot be obtained from these results, the data strongly suggest, *in this regime*, a scaling closer to $\lambda \sim M^{0.7}$ suggested by Birshtein and co-workers[17] than the $\lambda \sim M^{1.9}$ prediction of Fredrickson[18].

The bottle-brush diameter, D, can be defined as twice the root mean-square average of the distance between the grafted backbone bead and the end bead of the corresponding side-chain. However, important scaling information can first be obtained by looking at the closely related root mean-square average of the end-to-end distance, R_e, of the side chains (in our notation the grafted backbone bead is not a part of the side chain), shown in Fig. 4. Of course, the

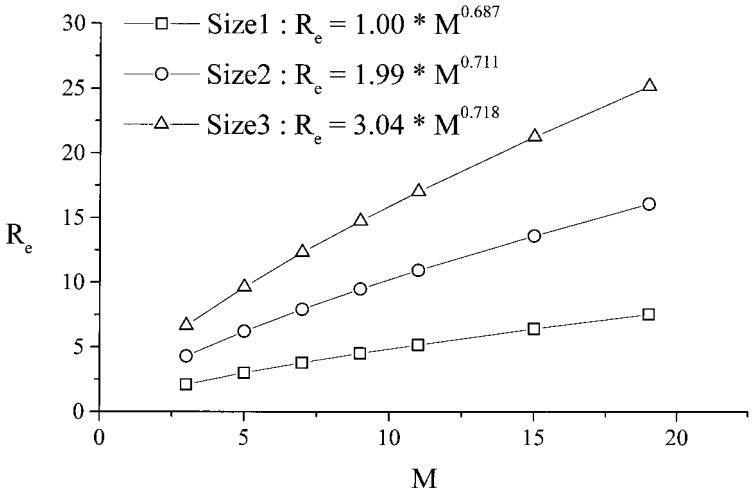

Fig. 4. End-to-end distance of the side chains of the bottle-brush structures as a function of the side-chain length, M. The error bars are smaller than the symbols used to present the data

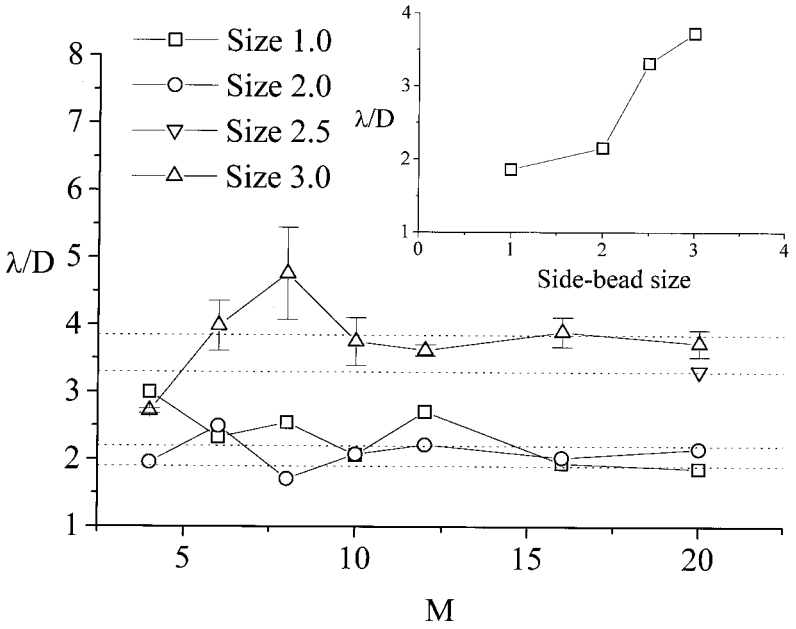

Fig. 5. The ratio of the persistence length, λ, over the bottle-brush diameter, D, as a function of the side-chain length, M. Inset shows the ratio as a function of the side-bead size for the largest bottle-brushes consisting of 50 side chains of 20 beads each

bottle-brush diameter will show a very similar behavior. The data have been fitted with a power law equation which leads to scaling predictions $R_e \sim M^{0.687}$ for side-bead size 1.0, $R_e \sim M^{0.711}$ for side-bead size 2.0, and $R_e \sim M^{0.718}$ for side-bead size 3.0. Since all the exponents are considerably larger than the 3d Self-Avoiding Walk (SAW) value of 0.588, it is clear that the excluded-volume effect is operational for the structures studied. In particular, the exponents for side-bead sizes 2.0 and 3.0 seem to suggest a leveling of to approximately 0.72, which happens to be exactly the same value as predicted by Birshtein and co-workers[17]. It is also close to the 2d SAW value of 0.75.

As pointed out before, the critical parameter for lyotropic behavior is the ratio between the persistence length and the bottle-brush diameter, which is presented in Fig. 5. Several striking observations can be made. Firstly, these results indicate that, in the regime studied, the ratio between the persistence length and the bottle-brush diameter is almost a constant as a function of M. Futhermore, this constant increases steadily with an increase in size of the side-chain beads, being about twice as large for the bottle-brushes having side-beads of size 3.0 than for the structures with side-beads of size 1.0. This behavior is illustrated in the inset of Fig. 5, which shows the ratio as a function of side-bead size for the largest structures consisting of 50 side chains of 20 beads each.

Based on the results presented, several conclusions can be drawn. In general, as observed before, the originally flexible backbone of a bottle-brush can be stretched considerably due to the excluded-volume interactions between the flexible side chains. However, in the regime studied, the increase in the persistence length is of the same order as the increase in the diameter as a function of the side-chain length. Therefore, in our freely-jointed chain model, lyotropic behavior cannot just be induced by using longer side chains. By contrast, increasing the side-bead size from 1 to 3 changed λ/D from about 1.9 to 3.9, which is still too small for nematic behaviour but suggests that, depending on the precise topology (for instance additional stiffness) of the side chains, it might become larger than 10, thus enabling lyotropicity. In fact, the results of Schmidt and co-workers[1–3] may provide an experimental example. Finally, our results do indicate that the length of the side chains is not really a crucial parameter, since the ratio between persistence length and diameter remained nearly constant already at very moderate side chain lengths.

Conclusions

In this paper, the equilibrium conformations of isolated molecular bottle-brushes consisting of a freely-jointed main chain of hard spheres (beads) grafted with freely-jointed side chains of hard spheres were considered. The effect of the side-chain topology was studied by varying the size of the side-chain beads between 1.0 and 3.0, expressed in units pertaining to the size of the backbone beads. Up to the largest structure studied, a main-chain of

100 beads and 50 side chains of 20 beads each, the ratio between the persistence length and the bottle-brush diameter remained approximately constant as a function of the side-chain length. On the other hand, the ratio depends strongly on the side-bead size, suggesting the importance of the side-chain topology. These findings suggest that in real bottle-brush systems, the ratio may become large enough for lyotropicity due to the proper side-chain chemistry.

Acknowledgement: The work has been supported by *Finnish Academy, Technology Development Centre (Finland)* and *Neste Foundation. Risto Nieminen* and *CSC Finland* is acknowledged for providing computing time. At Purdue this work is supported by *NSF grant CTS-9624268*.

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